(12) **APPLICATION**

(11) **20200087** (13) **A1**

(19) NO

NORWAY

(51) Int Cl.

B01D 53/00 (2006.01)
B01D 53/92 (2006.01)
F01N 3/02 (2006.01)
F25J 1/00 (2006.01)

Norwegian Industrial Property Office

(21)	Application nr	20200087	(86)	Int. application day and application nr
(22)	Application day	2020.01.23	(85)	Entry into national phase
(24)	Date from which the industrial right has effect	2020.01.23	(30)	Priority
(41)	Available to the public	2021.07.26		

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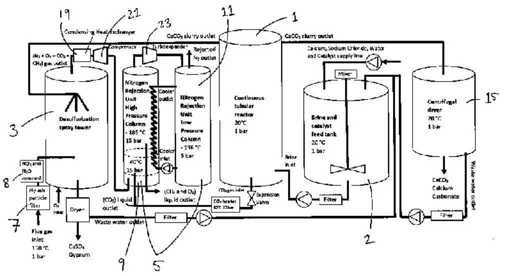
(54) Title **System for the Capture of CO2 in Flue Gas**
(57) Abstract

There is provided a nitrogen rejection unit for extracting nitrogen and carbon dioxide from a flue gas, the system comprising: a first container for holding a first volume of the flue gas at a first pressure and a first temperature that is below or equal to the condensation temperature of the carbon dioxide and greater than the condensation temperature of nitrogen; an outlet for removing the carbon dioxide as a liquid from the first container; means for transporting gaseous nitrogen from the first container to a second container and means for cooling the nitrogen such that the second container contains nitrogen at a second temperature that is below or equal to its condensation temperature such that at least some of the nitrogen in the second container is in liquid form; and means for guiding the liquid nitrogen from the second container through or around the first container to cool the material within the first container to the first temperature. There is also provided a system for capturing carbon dioxide in a flue gas, a method for extracting nitrogen from a flue gas, and a method for capturing carbon dioxide in a flue gas.



System for the Capture of CO_2 in Flue Gas

The present invention relates to a system for removal of CO_2 from flue gas, and particular to removal via mineralization of CO_2 from flue gas produced in a power plant.

Over the past several decades in particular, there has been increasing focus on the issue of global warming caused by carbon dioxide entering the atmosphere as a result of human activities. One of the main contributors to anthropogenic atmospheric carbon dioxide is electricity producing power plants, which burn fossil fuels. Alternative, cleaner, sources of energy such as wind, solar, or hydro are being investigated throughout the world and are now beginning to be widely implemented. It is arguable, however, that such means must be supplemented with other solutions if catastrophic warming is to be prevented. To this end, substantive research has been carried out on methods for the capture the carbon dioxide produced as an exhaust gas in power plants, as well as means of increasing the efficiency of combustion to reduce the level of carbon dioxide produced initially.

Power plants produce electricity via the combustion of fuels such as coal, petroleum, natural gas, biofuel, and coke. Heat generated by the combustion is used to create steam which drives a turbine to produce electricity. Burning natural gas as fuel, rather than coal, can help to reduce the level of pollutants in the resulting exhaust gas, however the levels are still high, which is clearly of concern.

Post-combustion solutions can be divided into those which capture carbon dioxide for storage underground, either in geological structures or in oil wells which have been drained of oil and lie empty, and those which use the carbon dioxide to produce stable products which can then be reused. The first solution is known as Carbon Capture and Storage (CCS) and the second as Carbon Capture and Utilization (CCU). Both are valuable, however storage of carbon dioxide in geological structures such as empty oil wells does run the risk of leakage, and this will of course result in the release of carbon dioxide into the atmosphere which the method aims to prevent. CCU, by contrast, can provide benefits in that by-products of the capture process are commercially valuable and can help to recoup some of the cost of including carbon capture processes in a plant.

Various chemical processes can convert carbon dioxide into alternative substances. One known method is to use an alkaline brine through which carbon dioxide is bubbled, resulting in the mineralization of the carbon dioxide to form a carbonate. If calcium ions are present in the brine, then calcium carbonate will be a product of the reactions occurring within the reactor. The carbon dioxide is therefore converted into an inert form rather than being released into the atmosphere.

In order to effectively fix carbon dioxide in this way, it is necessary to first separate out the various other elements of the flue gas. The table below outlines the composition of flue gas in a typical case. The substances making up the flue gas include dust and ash, as well as sulphur dioxide, methane, and nitrogen.

Substance	**Vol %**
N_2	72-77%
H_2O	8-10%
CO_2	12-14%
O_2	3-5%
SO_2	< 1%
NO_x	< 1%
CO	< 1%
N_2O	< 1%
CH_4	< 1%

Typical Flue Gas Composition

Filters are often used in order to remove components of the flue gas or elements can be separated using cryogenic separation techniques (liquification of some substances within the gas by cooling). Sulphur oxides (such as sulphur dioxide) can be removed from the flue gas via a process referred to as “wet scrubbing” or wet flue gas desulphurization. Here, a slurry containing absorbent, either in solution or in suspension, is sprayed into the flue gas within a chamber so that elements of the slurry react with the sulphur. Components forming the slurry need to be sourced and transported to the power plant which of course adds to running costs. Dry processes for desulphurization can also be used, however these tend to be less efficient.

The below description focusses on the mineralization of carbon dioxide by bubbling it through an alkaline brine to convert it into an inert substance. Here, a reaction with metal cations takes place after hydrogenation of the carbon dioxide in order to form carbonates. If calcium cations are present, then calcium-based carbonates will be formed. If magnesium or iron cations are present, then magnesium or iron-based carbonates will be formed, and so on. The cations used will depend on what the desired final product of the reaction. Calcium carbonate slurry, which is a product of the reaction with calcium ions, can be dried to form calcium carbonate which is used widely and so calcium cations in solution will generally be a good choice, but any metal cation or combinations of metal cation can be used.

The reduction of carbon dioxide emissions is extremely beneficial to a company running a power plant, both in terms of the effect on the environment and because of the high levels of tax payable by companies on emissions. A problem with using this type of ex-situ mineralization for the conversion of carbon dioxide is that the reaction rate of the hydrogenation is slow, increasing running costs to impractical levels. There is therefore a balance to be struck between these factors if the plant is to be cost-effective. US Patent Number 9,789,439 (hereafter Siller) describes the use of solid metal materials (and in particular of nickel nanoparticles) to increase the rate of hydration of carbon dioxide prior to reaction with the metal cations in solution. Application of this technology to the carbon fixing process can greatly reduce the cost of implementation.

Carbon capture can reduce carbon dioxide production in a power plant fairly effectively, and the use of solid metal catalysts can reduce the cost of applying such techniques. These methods are, however, still expensive because of the requirement of additional equipment required to pump or heat and cool the different components. Improvements in the efficiency of such processes are desired.

According to a first aspect of the present invention, there is provided A nitrogen rejection unit for extracting nitrogen and carbon dioxide from a gas, the system comprising: a first housing for holding a first volume of the gas at a first pressure and a first temperature that is below or equal to the condensation temperature of the carbon dioxide and greater than the condensation temperature of nitrogen; an outlet for removing the carbon dioxide as a liquid from the first housing; means for transporting gaseous nitrogen from the first housing to a second housing and means for cooling the nitrogen such that the second housing holds nitrogen at a second temperature that is below or equal to the condensation temperature of nitrogen; and means for guiding liquid nitrogen from the second housing through or around the first housing to cool the material within the first housing to the first temperature.

In embodiments, there is provided a nitrogen rejection unit according to claim 1, wherein the gaseous nitrogen expands as it passes from the first housing to the second housing such that material in the second housing is at a second pressure that is higher than the first pressure.

In embodiments, energy from the expansion of the gaseous nitrogen as it passes from the first housing to the second housing is used to compress the gas entering the first housing.

In embodiments, the gaseous nitrogen passes through an expansion turbine as it passes from the first container to the second container, and the expansion turbine is configured to drive a compressor for compressing the first volume of the flue gas to the first pressure.

In embodiments, liquid nitrogen is flows from the second housing through the first housing along a pipe that forms a tortuous path and then back to the second housing.

In embodiments, the nitrogen rejection unit comprises a compressing heat exchanger for heating and drying the gas entering the system.

In embodiments, the material within the first housing is held at a pressure of around 15 bar and the material within the second housing is held at a pressure of around 5 bar.

In embodiments, the material within the second housing is cooled to a temperature of around -196°C.

In embodiments, the material within the first housing is cooled to a temperature of around -185°C.

According to a second aspect of the present invention, there is provided a system for capturing carbon dioxide in a flue gas, the system comprising: a desulphurization unit for removing sulphur dioxide from the flue gas; a nitrogen rejection unit of the first aspect; a reactor unit containing an alkaline brine and a catalyst and having an inlet for receiving carbon dioxide from the nitrogen rejection unit for the reaction of the carbon dioxide to form a carbonate slurry.

In embodiments, the desulphurization unit is configured to receive at least a portion of the carbonate slurry produced in the reactor unit for use in wet scrubbing of the flue gas to remove the sulphur dioxide.

In embodiments, the system comprises a brine feed tank configured to receive and mix the constituents of the alkaline brine with the catalyst before transport to the reactor unit.

In embodiments, the system comprises a condensing heat exchanger configured to remove waste water from the flue gas before it enters the nitrogen rejection unit, wherein the system comprises means to transport the waste water to the brine feed tank.

In embodiments, the system comprises means for extracting water from at least portion of the calcium carbonate slurry produced in the reactor unit and to transport the extracted water to the brine feed tank for mixing.

In embodiments, the system comprises one or more filters for removing ash and NO_x from the flue gas before it enters the desulphurization unit.

According to a third aspect of the present invention, there is provided a method for extracting nitrogen from a flue gas comprising nitrogen and carbon dioxide, the method comprising: compressing, using a compressor, a volume of the flue gas to a first pressure and cooling it to a first temperature that is below or equal to the condensation temperature of carbon dioxide and greater than the condensation temperature of nitrogen; removing the carbon dioxide as a liquid from the first volume; passing the nitrogen from the first volume to a second and cooling it to a second temperature that is below or equal to the condensation temperature of nitrogen; removing liquid nitrogen from the second volume passing at least some of the liquid nitrogen from the second volume through or around the first volume to cool the material therein.

In embodiments, the nitrogen is passed from the first volume to the second volume through an expansion turbine such that it reaches a second pressure that is higher than the first pressure, and wherein the expansion turbine is used to drive the compressor.

According to a fourth aspect of the present invention, there is provided a method for capturing carbon dioxide in a flue gas, the method comprising: removing sulphur dioxide from the flue gas in a desulphurization unit; separating nitrogen and carbon dioxide from the flue gas using the method of the third aspect; transporting the extracted carbon dioxide to a reactor unit containing an alkaline brine; and converting the carbon dioxide in the reactor unit to a carbonate.

According to a fifth aspect of the present invention, there is provided a method for capturing carbon dioxide in flue gas, the method comprising: removing sulphur dioxide from the flue gas by wet scrubbing in a desulphurization unit; removing nitrogen from the flue gas in a nitrogen rejection unit and separating carbon dioxide from the flue gas for input into a reactor unit with an alkaline brine and a solid metal catalyst; mineralizing the carbon dioxide in the reactor unit to form a carbonate slurry, wherein the initial hydrogenation of the carbon dioxide is catalyzed by the solid metal catalyst; and transporting at least some of the carbonate slurry to the desulphurization unit for use in wet scrubbing of the flue gas to remove the sulphur dioxide.

In embodiments, the solid metal catalyst comprises nickel nanoparticles.

In embodiments, calcium is added to the alkaline brine and the carbonate slurry produced is calcium carbonate slurry.

Embodiments of the present invention will now be described, by way of example only, with reference to the following diagrams wherein:

Figure 1 shows a diagram of a carbon dioxide removal system;

Figure 2 shows a perspective view of a removal system, including reactor tanks and brine feed tanks;

Figure 3 shows cross-sectional views of a reactor (left) and a bring feed tank with mixer (right);

Figure 4 is a flow-chart illustrating the re-use of products in the system;

Figure 5 shows some of the components of a nitrogen rejection unit;

Figure 6 is a flow chart illustrating the mass balance of the carbon capture process;

Figure 7 is a flow chart illustrating the energy balance for the carbon capture process.

Figure 1 illustrates a system for the removal of carbon dioxide from flue gas including the various units or sub-systems coupled together to form the larger apparatus. Units refer to the smaller parts of the whole, including each of the desulphurization unit 3 (which may be a spray tower as shown in the figure), the reactor unit 1 (which may be a continuous tubular reactor), the nitrogen rejection unit 5, and the brine feed tank 2. Flue gas enters the desulphurization unit 3 through one or more filters 7 which act to remove particulates such as fly ash. These filters may be electrostatic precipitator filters. Also prior to entering the spray tower in a further sub-system indicated as numeral 8 in the figure (or less preferably within the tower) the gas may undergo a selective catalytic reduction reaction using ammonia to remove NOx from the gas in the following reaction:

$$4\ NO_X\ (g) + 4\ NH_3\ (l) + O_2\ (g) \rightarrow 4\ N_2\ (g) + 6\ H_2O\ (l)$$

Before, after, or concurrently with the above reaction proceeding (also within subsystem 8), removal of N_2O may be carried out in another selective catalytic reduction reaction, this time using methane in the following reaction:

$$2\ N_2O\ (g) + CH_4\ (g) \rightarrow 2\ N_2\ (g) + CO_2\ (g) + 2\ H_2\ (g)$$

The methane may be already present within the flue gas, may be redirected from the output of the high-pressure column of the nitrogen rejection unit 5 (see below), or may be sourced externally.

Within the spray tower 3, sulphur dioxide is removed from the gas via a wet scrubbing process using calcium carbonate slurry. Elements of the calcium carbonate slurry in the form of droplets react with the SO_2 resulting in the production of $CaSO_42H_2O$ (gypsum slurry) in the following reactions:

$$SO_2\ (g) + CaCO_3\ 0{,}5H_2O\ (l) \rightarrow CaSO_3\ 0{,}5H_2O\ (l) + CO_2\ (g)$$
$$CaSO_3\ 0{,}5H_2O\ (l) + 0{,}5\ O_2\ (g) + 1{,}5H_2O\ (l) \rightarrow CaSO_4\ 2H_2O$$

The gypsum slurry which produced as output from the desulphurization unit 3 is dried to produce commercial grade gypsum which is then transported from the plant for sale and/or use. Water extracted during the drying process can be filtered and reused within the system as will be described in more detail below.

Flue gas with SO_2 removed passes through a condensing heat exchanger to remove water vapor before it is pressurized to 15 bar and fed into a two-column nitrogen rejection unit 5 comprising each of a high-pressure column 9 and low-pressure column 11. Here, nitrogen is separated off from the rest of the gas by cooling the gas to liquify carbon dioxide, methane and oxygen. The pressurized nitrogen gas is fed into a turboexpander to depressurize the nitrogen gas from 15 bar to 5 bar and turn it into liquid nitrogen in the process. The high-pressure nitrogen gas propels a turbine in a non-combustion process which in turn drives the compressor used to pressurize the flue gas from 1 bar to 15 bar before it is fed into the high-pressure column. This makes the nitrogen rejection unit particularly energy efficient to operate.

Details of the nitrogen rejection unit 5 are provided below. Because the nitrogen rejection unit works by cooling the gas until methane, oxygen, and carbon dioxide become liquid, these other components of the flue gas can be separated from the nitrogen and removed as liquid from the unit. Liquid methane is useful as a biofuel additive, for example, and can be stored or transported to this end. Phase changes occurring in the nitrogen rejection unit are as follows:

$$N_2\ (g) + O_2\ (g) + CO_2\ (g) + CH_4\ (g) \rightarrow N_2\ (l) + O_2\ (l) + CO_2\ (l) + CH_4\ (l)$$

The following table lists condensation temperatures for some components of the flue gas. The temperatures listed for nitrogen, methane, and oxygen are those at atmospheric pressure. In the case of carbon dioxide, the pressure also needs to be above 5 bar in order for it to be in liquid form and the condensation temperature at 5 bar pressure is listed. CO_2 cannot be in its liquid form at atmospheric pressure.

Constituent of the Flue Gas	Condensation Temperature (°C)
Nitrogen	-196
Carbon Dioxide	-56.6 (-57) (-40 at min. 10 bar and turns solid below -80)
Methane	-162
Oxygen	-182.96 (~ -183)

Methane, oxygen, and carbon dioxide are liquified by using liquid nitrogen as a coolant in a closed loop 2-stage cooler in the high-pressure column 9. Carbon Dioxide will liquify at - 40°C when pressurized to a minimum of 10 bar and will be and syphoned off from the high-pressure column through an outlet as shown in figure 1 in the 1st stage cooler. It is important to syphon off the liquid Carbon Dioxide before it cools down to below -80°C and becomes solid (ice). Methane and oxygen will liquify at respectively -162°C and -183°C and will be and syphoned off from the high-pressure column through another outlet as shown in figure 1 in the 2nd stage cooler.

Liquid carbon dioxide is heated up to from -40°C to 80°C turning it to gas and increasing the pressure to 20 bar before being passed through an expansion valve to the reaction unit, reducing the temperature and pressure to a temperature of 20°C at 1 bar. In the reaction unit it is mixed with artificial brine having the same temperature and pressure (20°C and 1 bar).

The reactor unit may be a continuous tubular reactor as shown, however the shape of the housing within which reactions to convert carbon dioxide to carbonate take place is not limited to any particular shape. The housing must be able to contain the reactants at the desired temperature and pressure and must include inlets for reactants and outlets for products. Alkaline brine and the catalysts required for the hydrogenation reaction are fed from a feed tank 2 held at between 10°C and 30°C, more preferably between 15°C and 25°C and more preferably at around 20°C and at a pressure of between 0.5 and 2 bars and preferably at 1 bar of pressure. The tubular reactor 1 is held within the same ranges of temperatures and pressures as the feed tank 2 and is preferably held at the same temperature and pressure as the feed tank.

Within the tubular reactor, the following reactions take place if calcium is used:

$$CO_2\ (g) + CaCl_2 \times 2H_2O\ (l) + 2\ NaOH\ (l) \rightarrow CaCO_3\ (s) + 3\ H_2O\ (l) + 2\ NaCl\ (l)$$

The alkaline brine may be from desalination or may be artificially produced. In the example shown, a catalyst (which may comprise nickel nanoparticles), sodium chloride, and calcium are added to water (some of which may be produced in drying slurry formed in one or more of the desulphurization unit or the reactor unit) and transported to the brine feed tank. Some additional fresh water may need to be added along with the waste water to achieve the desired consistency. The concentration of NaCl may, in some embodiments, be between 0.005 mol/litre and 0.05 mol/litre, preferably 0.02 mol/litre of the water. The ratio of brine (including catalysts and cations) to CO_2 within the tubular reactor should be maintained at between 3:1 and 5:1, preferably at around 4:1. This can be done by monitoring the rate of flow of the flue gas or of the material passing into the reactor unit at the inlet and adjusting the flow rate of material from the brine feed tank to the reactor unit accordingly. This could be achieved, for example, by adjusting the operation of a pump moving fluid from the brine feed tank to the tubular reactor in response to sensors measuring a flow rate either of the flue gas entering the system or of the material at any point within the apparatus prior to it reaching the inlet to the reactor tank.

Again, this method includes reuse of waste products for other means, improving efficiency and reducing cost of implementing the process. Mixing of the elements within the feed tank 2 may be aided by mechanical mixing means, an example of which is shown in figure 3 and indicated with numeral 13.

One of the products of the reactions occurring in the reactor unit in a case where calcium ions are present is calcium carbonate slurry. Some (for example between 80% and 95%) of this slurry may be dried out, preferably using a centrifugal dryer 15 as shown at between 15°C and 25°C, preferably at 20°C, and at a pressure between 0.5 bar and 2 bar, preferably at 1 bar pressure. Water removed from the slurry can be redirected, possibly through one or more filters to ensure that the water does not contain additional particulates and can flow back to the feed tank to be added to the brine held therein.

The calcium carbonate resulting from the drying step represents a useful commercial product and can be stored or sold in order to recoup some of the money used to implement the system. A portion of the calcium carbonate slurry may be transported from the reactor where it is formed to the spray tower to be used in the desulphurization process. In embodiments, between 3% and 20%, and preferably between 5% and 10%, of the calcium carbonate slurry produced in the reactor unit is transported to the spray tank for reuse in the desulphurization process (and the rest dried and the commercial grade calcium carbonate transported for sale or use).

All of the calcium carbonate slurry required for the desulphurization process can therefore be sourced from the output from the reactor unit. This way, calcium carbonate does not need to be sourced, paid for, and transported to the plant, which further increases the efficiency of the process. There is a level of synergy between the use of a solid metal catalyst and re-use of carbonate slurry formed as a result of the catalysed reaction in the desulphurization. The conversion rate from carbon dioxide to calcium carbonate required to supply the desulphurization process with sufficient amounts of calcium carbonate slurry can be obtained by the use of a solid metal catalyst, thus the increase in the efficiency of the whole process achieved by using both techniques is greater than sum of the individual increases in efficiency which would be achieved by the use of each technique alone.

Figure 2 shows a perspective view of an apparatus for carbon capture. The figure is simplified and excludes various components such as check and gate valves, pipe supports, and process sensors, all of which will be present in an embodiment. The apparatus here includes four tubular reactor tanks fed by four brine feed tanks. A reactor unit, therefore, may comprise two or more reactor tanks, just as the desulphurization unit may comprise two or more spray towers. A number of brine feed tanks may be present to form a brine feed unit. Two vacuum belt dryers 17 are included along with two screw separators 15 in the example shown, which receive calcium carbonate slurry from the reactor tank(s) and remove the water therefrom. An alternative simplified design uses only centrifugal separators to separate the water from the calcium carbonate. These centrifugal separators use gravitational and/or centrifugal force to separate out the liquid from the calcium carbonate in the calcium carbonate slurry. Electromagnets may be installed, for example in the inlet leading to the centrifugal separator or to the vacuum dryer/screw separator, to capture metal catalyst particles for re-use in the conversion process. Such electromagnets (or other means for separating out a catalyst from waste material leaving the reactor unit) can be used in any system. If magnetic means are used, these can be used in any system where solid metal or other magnetic catalysts are used. Because the catalyst particles are formed from solid metal, these are attracted to the magnets and captured for transport back to the brine feed tank or back to the reactor unit.

The number of tanks, separators, and/or dryers is not fixed. Although in the figure one brine feed tank is connected to and feeds brine to one reactor tank, this also need not be the case and one of the feed tanks may feed brine to two or more of the reactor tanks if desired. The decision as to how many tanks of each type are required will be based largely on a balance of the cost with the required capacity of the system. Pipes carry flue gas, which has been mixed with the alkaline brine to the reactor unit for mineralisation. Additional inlets into the separators are at the base in this case and are not visible in the figure. Some of the slurry output from the reactor unit passes through the dryers and screw separators or the centrifugal separator and the extracted water is transported back to the brine feed tank through pipes. The screw separator or the centrifugal separator will each provide enough pressure to force the extracted water back into the brine feed tank. Commercial grade calcium carbonate is output as a product.

Figure 3 shows cross sections of a tubular reactor (left) and a brine feed tank (right). The tanks are each cylindrical in the examples shown but need not be so provided that they can sufficiently contain the reactants and products as required. The tubular reactor tank includes a water vapour outlet, which may help to prevent any unwanted increase in pressure. The tubular reactor tank also includes a Pressure Safety Valve which will release the pressure in the reactor tank at a set pressure, in the event of excessive pressure from any of the inlets (carbon dioxide or brine). The water vapour can be transported back to the flue gas chimneys or can be released directly from the top of the reactor tank without being reincorporated in the system. The brine feed tanks include one or more inlets for waste water extracted from the $CaCO_3$ slurry after mineralization of carbon and for the brine and catalyst components and outlets for drainage and to carry brine and catalyst to the tubular reactor unit. The feed tanks each contain an electrical mixer 13 powered by a motor and comprising several sets of spinning arms to aid mixing of the component prior to transport to the reactor unit.

Pumps are included in the system and these function to move material between the units. A large capacity pump, for example, is used to move brine from the brine feed tank and into the reactor unit.

The housings for the brine feed tank, tubular reactor, and spray tank (if present) as well as the tubes carrying material between the tanks or units are preferably manufactured completely or partially from stainless steel. A typical reactor tank may be upwards of 15 feet high (around 20 ft high) which may necessitate construction of the apparatus on-site near to the power plant. Supply and return pipelines, transporting flue gas from the power plant and waste products from the power plant, may also be formed from stainless steel. Additional structure or frames, which may again be formed from stainless steel, can be used to protect the reactor tanks, as well as the brine feed tank and spray tank if required.

The process shown in figure 1 and described above adds additional efficiency to the carbon capture procedure and reduces costs in two ways. Firstly, use of a solid metal catalyst to increase the rate of hydrogenation of the carbon dioxide within the tubular reactor means that the whole process can happen quicker, which of course means that pumps, condensers, heaters, and so on do not need to be operated for such long periods. This greatly saves on running costs.

Secondly, the process includes the reuse of waste or output products of sub-processes as input to other sub-processes within the overall system. Figure 4 is a flow chart omitting some parts of the process but illustrating in particular the idea of reusing the output of one sub-process or unit as the input to another.

There are three main parts of the system which capitalise on the possibility of recycling what would traditionally be considered as a waste product. Rather than these substances simply being disposed of or put to other unrelated uses, they are re-used within the system itself. The choice of the combination of reactants used for each of the units or sub-systems (the reactor unit, brine feed tank, nitrogen rejection unit, and desulphurization unit in an example) facilitates this recycling of products because the outputs to certain of these units are also the inputs to other parts of the system where possible.

Water that is passed into the feed tank and used to form the brine which supports hydrogenation and mineralisation of the carbon dioxide is sourced from the output of one or more of the desulphurization unit and the reactor unit. Although some water may be sourced externally if required, at least some and potentially most or all of the water input to the feed tank is extracted during drying of the output from the desulphurization unit to form gypsum, and/or extracted during drying of the slurry that is output from the reactor to form calcium carbonate. This extracted waste water may be filtered before being passed back into the feed tank as shown. In order that the dried calcium carbonate meets requirements in terms of quality for commercial sales, a large capacity vacuum plate dryer or a centrifugal dryer may be required to properly extract water from the slurry which is output from the reactor tank.

Some of the calcium carbonate slurry, which is the product of reactions taking place within the reactor, is not disposed of but is directed back to the spray tower and used in the wet scrubbing process for the removal of SO_2 from the flue gas entering the system.

Additional, external, sources of water and calcium carbonate slurry may be included for input to the feed tank and the desulphurization unit, although these may not (and generally will not) be required. These additional input means can also be used if waste products are not being produced at the rate required, for example during start-up of the system if there is a lag between switching on of the system and the start of production of waste products from later sub-processes which are recycled for use in earlier processes, such as the output from the tubular reactor section which is reused in the desulphurisation step.

The nitrogen rejection unit 5 will now be described in more detail. The apparatus uses cryogenic distillation to separate out the various constituents of the gas. This works particularly well within the overall system for carbon capture described herein because of the need to extract CO_2 for input to the reaction chamber. Other gases are also syphoned off and can be stored or transported for use. Methane, as mentioned, can be a useful additive for biofuels and liquid nitrogen is used widely for cooling. Although the apparatus is particularly suitable for use in the carbon capture system described herein, the nitrogen rejection unit 5, including high pressure column 9 and low-pressure column 11, can be used in any carbon capture process where flue gas is required to be separated into its component parts. The system can indeed be used anywhere that nitrogen needs to be extracted from a gas and the constituents of the gas separated out.

The nitrogen rejection unit 5 is illustrated in figure 5. The input shown is flue gas, treated to remove ash, NO_x and SO_x as described above. As mentioned, the input may be any nitrogen containing gas. Other liquid substances in addition to methane and carbon dioxide may then be syphoned from the high-pressure column once they have become liquid.

In this case, the gas input into the system or sub-system is treated flue gas containing gaseous nitrogen, oxygen, carbon dioxide, and water (which may be in the form or water vapour). This gas passes first through a dryer 19, which may be a condensing heat exchanger, within which water vapour is removed from the gas. The dry gas now containing nitrogen, oxygen, methane and carbon dioxide, is passed to a compressor 21 which increases the pressure of the gas, such as to around 10 bar to 30 bar, preferably 20 bar to 30 bar, and most preferably to 25 bar, before passing it into the high-pressure column. The appropriate one-way valves are included (not shown) in order to maintain material within the high-pressure portions when desired. Additional pumps may also be required to move materials between and through parts of the system and these are also not shown. Where pressure is referred to, this refers to the pressure produced by the mix of gases and liquids that will be within the tanks or vessels including pipes and valves in the process. The pressure will remain relatively constant for each tank or vessel, including the high and low-pressure columns of the nitrogen rejection unit throughout the process.

Within the high-pressure column 9 the gas, held at between 5 bar and 30 bar, preferably at between 10 bar and 20 bar, more preferably at between 13 and 17 bar, and most preferably at around 15 bar, is cooled using liquid nitrogen circulated through the column down to a temperature of between -180°C and -190°C, preferably between -182°C and -188°C, most preferably at around -185°C. The cooling will take place in two sequential coolers, 1st stage cooler which will cool the gas down to -40°C, which will liquify carbon dioxide and allowing it to be syphoned off. The 2nd stage cooler will cool the remaining gas down to -184°C, liquifying methane and oxygen and allowing it to be syphoned off. This is below the temperature at which carbon dioxide becomes solid (ice) at the pressure of the column. The two-stage cooling process will turn all of the methane, carbon dioxide, and oxygen in the flue gas into liquid form, which can then be easily extracted from one or more outlets. These outlets will generally be at or near to the base of the high-pressure column. In order to separate the extracted materials, the temperature of the liquid outlet from the high-pressure column of the nitrogen rejection unit is increased incrementally so that the vaporization temperature of each of the gases therein is passed in turn allowing these to be outgassed separately from one another. Alternatively, different outlets can be used at different heights depending on the density of each liquid.

Only nitrogen remains in its gaseous form, and this is transported from the high-pressure column 9 to the low-pressure column 11 through an outlet which will generally be located at or near to the top of the high-pressure column. As the nitrogen gas passes from the high-pressure column to the low-pressure column it expands, and energy from the expansion drives a non-combustion turbine which is used to drive the compressor 21. The compressor acts to increase the pressure of the gas entering the nitrogen rejection system. An expansion turbine or turboexpander 23 may be used for this purpose.

The nitrogen is cooled further by expansion in the turboexpander to a temperature of between -200°C and -190°C, more preferably between -198°C and -194°C, and most preferably at -196°C. Because of the pressure, which is still above atmospheric pressure, the nitrogen will now be in its liquid form. Rather than including separate cooling means or using nitrogen that is sourced externally, the nitrogen from the flue gas (which is now liquid nitrogen) is recycled and used as cooling fluid for the high-pressure column by passing it through one or more tubes 25 running into and through or around the high-pressure column. Excess liquid nitrogen is syphoned off and away from the system for storage or use elsewhere. Clearly, the structure of these cooling tubes is important, and a high surface area is desired for heat transfer.

Thin, long, and winding tubes may be used, or even a plate structure within the high-pressure column through which liquid nitrogen is passed.

Use of the expansion turbine to drive the compressor and recycling of the liquid nitrogen to cool the high-pressure column are unique features. As a result of their inclusion, less energy is required to be input to the nitrogen rejection system and the efficiency of the overall process is increased. This lowers the operational cost of which is of paramount importance to companies seeking to reduce their carbon footprint using a process which remains commercially viable.

The overall system described is theoretically capable of converting 100% of the carbon dioxide present in the flue gas to carbonates reducing the additional tax burden due to CO_2 emissions to zero. In addition, the carbonate product may be commercial grade calcium carbonate which can be sold for use in the building industry recouping at least some of the cost of implementing the carbon capture technology described above.

Figure 6 illustrates the total mass balance of the process described above for a typical coal burning power plant. In this case numbers are based on the Belchatow power plant in Poland, which operates at 5035 MW (or at around 5000MW). The numbers will vary depending on the size of each plant.

The following table illustrates the mass flow into the carbon capture apparatus for each of the constituent parts of the flue gas in a plant operating at around 5000MW, such as Belchatow. The numbers provided in both the table and the figure are calculated on the assumption that 100% carbon dioxide mineralisation can be achieved. The mass flow in practice will be distributed across an array of apparatuses, each serving one combustion chamber within the plant. In the case of the Belchatow plant, in order to deal with the rate of production of CO_2 it will likely be necessary for two reactor tanks to be present serving each of the combustion chambers.

Substance	q_m (kg/min)
N_2	300 000
H_2O	83 100
CO_2	60 000
O_2	13 200
SO_2	60
NO_x	60
CO	60
N_2O	60
CH_4	13 680
Ash	41 100

This following table lists ratios of mass flow for different substances. These values (unlike the absolute mass flow numbers in the table above) should not vary much between plants.

Substance	Ratio of Mass Flow Values
N_2/CO_2	5
H_2O/CO_2	1.385
O_2/CO_2	0.22
SO_2/CO_2	0.001
NO_x/CO_2	0.001
CO/CO_2	0.001
N_2O/CO_2	0.001
CH_4/CO_2	0.228
Ash/CO_2	0.685

The total process energy balance is shown in figure 7, again based on the Belchatow plant which has 13 combustion chambers. Numbers in the figure are calculated based on the following specific heat capacity measurement for each substance.

Substance	Specific heat capacity c_p (J/kg C)
Flue gas	1 243
N_2	1 004
H_2O	4 200
CO_2	750
O_2	900
SO_2	633
NO_x	975

CO	1 047
N_2O	995
CH_4	2 225
$CaCO_4$	8 343
$CaSO_3$	1 090
Brine	2 300

More than one carbon capture system, and preferably two such systems, may be installed to serve each of the combustion chambers in a power plant.

The carbon capture system described above is more efficient than prior solutions because, aside from the use of solid metal catalysts to increase the speed of reactions occurring within the reactor sub-system, wherever possible waste substances and energy are recycled and used in other parts of the system. This is true in the case of the spray tower, where waste slurry from the reactor is used to remove SO_2 from incoming flue gas, in the case of the nitrogen rejection unit, where nitrogen extracted from the flue gas itself provides energy required for compression as it expands and is reused for cooling of the incoming gases. Waste water is also recycled where possible to produce the slurry that is input into the reactor.

Claims

1. A nitrogen rejection unit (5) for extracting nitrogen and carbon dioxide from a gas, the system comprising:

   a first housing (9) for holding a first volume of the gas at a first pressure and a first temperature that is below or equal to the condensation temperature of the carbon dioxide and greater than the condensation temperature of nitrogen;

   an outlet for removing the carbon dioxide as a liquid from the first housing (9);

   means for transporting gaseous nitrogen from the first housing to a second housing (11) and means for cooling the nitrogen such that the second housing holds nitrogen at a second temperature that is below or equal to the condensation temperature of nitrogen; and

   means for guiding liquid nitrogen from the second housing through or around the first housing to cool the material within the first housing to the first temperature.

2. A nitrogen rejection unit (5) according to claim 1, wherein the gaseous nitrogen expands as it passes from the first housing (9) to the second housing (11) such that material in the second housing is at a second pressure that is higher than the first pressure.

3. A nitrogen rejection unit (5) according to claim 2, wherein energy from the expansion of the gaseous nitrogen as it passes from the first housing (9) to the second housing (11) is used to compress the first volume of gas entering the first housing.

4. A nitrogen rejection unit (5) according to claim 3, wherein the gaseous nitrogen passes through an expansion turbine (23) as it passes from the first housing (9) to the second housing (11), and the expansion turbine is configured to drive a compressor (21) for compressing the first volume of the gas to the first pressure.

5. A nitrogen rejection unit (5) according to any of claims 1 to 4, wherein liquid nitrogen is flows from the second housing (11) through the first housing (9)

along a pipe (25) that forms a tortuous path and then back to the second housing.

6. A nitrogen rejection unit (5) according to any of claims 1 to 5, comprising a compressing heat exchanger (19) for heating and drying the gas entering the system.

7. A nitrogen rejection unit (5) according to claim 2, wherein the material within the first housing (9) is held at a pressure of around 15 bar and the material within the second housing (11) is held at a pressure of around 5 bar.

8. A nitrogen rejection unit (5) according to any of claims 1 to 7, wherein the material within the second housing (11) is cooled to a temperature of around -196°C.

9. A nitrogen rejection unit (5) according to any of claims 1 to 7, wherein the material within the first housing (9) is cooled to a temperature of around -185°C.

10. A system for capturing carbon dioxide in a flue gas, the system comprising:
a desulphurization unit (3) for removing sulphur dioxide from the flue gas;
a nitrogen rejection unit (5) according to of any of claims 1 to 9;
a reactor unit (1) containing an alkaline brine and a catalyst and having an inlet for receiving carbon dioxide from the nitrogen rejection unit (5) for the reaction of the carbon dioxide to form a carbonate slurry.

11. A system according to claim 10, wherein the desulphurization unit (3) is configured to receive at least a portion of the carbonate slurry produced in the reactor unit (1) for use in wet scrubbing of the flue gas to remove the sulphur dioxide.

12. A system according to any of claims 10 and 11, comprising a brine feed tank (2) configured to receive and mix the constituents of the alkaline brine with the catalyst before transport to the reactor unit (1).

13. A system according to claim 12, comprising a condensing heat exchanger (19) configured to remove waste water from the flue gas before it enters

the nitrogen rejection unit (5), wherein the system comprises means to transport the waste water to the brine feed tank (2).

14. A system according to any of claims 10 to 13, wherein the system comprises means for extracting water from at least portion of the calcium carbonate slurry produced in the reactor unit (1) and to transport the extracted water to the brine feed tank (2) for mixing.

15. A system according to any of claims 10 to 14, comprising one or more filters (7) for removing ash and NO_x from the flue gas before it enters the desulphurization unit (3).

16. A method for extracting nitrogen from a gas comprising nitrogen and carbon dioxide, the method comprising:

compressing, using a compressor (21), a volume of the gas to a first pressure and cooling it to a first temperature that is below or equal to the condensation temperature of carbon dioxide and greater than the condensation temperature of nitrogen and transferring the volume of gas to a first housing (9);

removing the carbon dioxide as a liquid from the first housing (9);

passing the nitrogen from the first housing to a second housing (11) and cooling it to a second temperature that is below or equal to the condensation temperature of nitrogen;

removing liquid nitrogen from the second housing (11) and passing at least some of the liquid nitrogen from the second housing (11) through or around the first housing (9) to cool the material therein.

17. The method according to claim 16, wherein the nitrogen is passed from the first housing (9) to the second housing (11) through an expansion turbine (23) such that it reaches a second pressure that is higher than the first pressure, and wherein the expansion turbine (23) is used to drive the compressor (21).

18. A method for capturing carbon dioxide in a flue gas, the method comprising:

removing sulphur dioxide from the flue gas in a desulphurization unit (3);

separating nitrogen and carbon dioxide from the flue gas using the method of any of claims 16 and 17;

transporting the extracted carbon dioxide to a reactor unit (1) containing an alkaline brine; and

converting the carbon dioxide in the reactor unit (1) to a carbonate.

19. A method for capturing carbon dioxide in flue gas, the method comprising:

removing sulphur dioxide from the flue gas by wet scrubbing in a desulphurization unit (3);

removing nitrogen from the flue gas in a nitrogen rejection unit (5) and separating carbon dioxide from the flue gas for input into a reactor unit (1) with an alkaline brine and a solid metal catalyst;

mineralizing the carbon dioxide in the reactor unit (1) to form a carbonate slurry, wherein the initial hydrogenation of the carbon dioxide is catalyzed by the solid metal catalyst;

and transporting at least some of the carbonate slurry to the desulphurization unit (3) for use in wet scrubbing of the flue gas to remove the sulphur dioxide.

20. The method according to claim 19, wherein the solid metal catalyst comprises nickel nanoparticles.

21. The method according to any of claims 19 and 20, wherein calcium is added to the alkaline brine and the carbonate slurry produced is calcium carbonate slurry.

Fig. 1

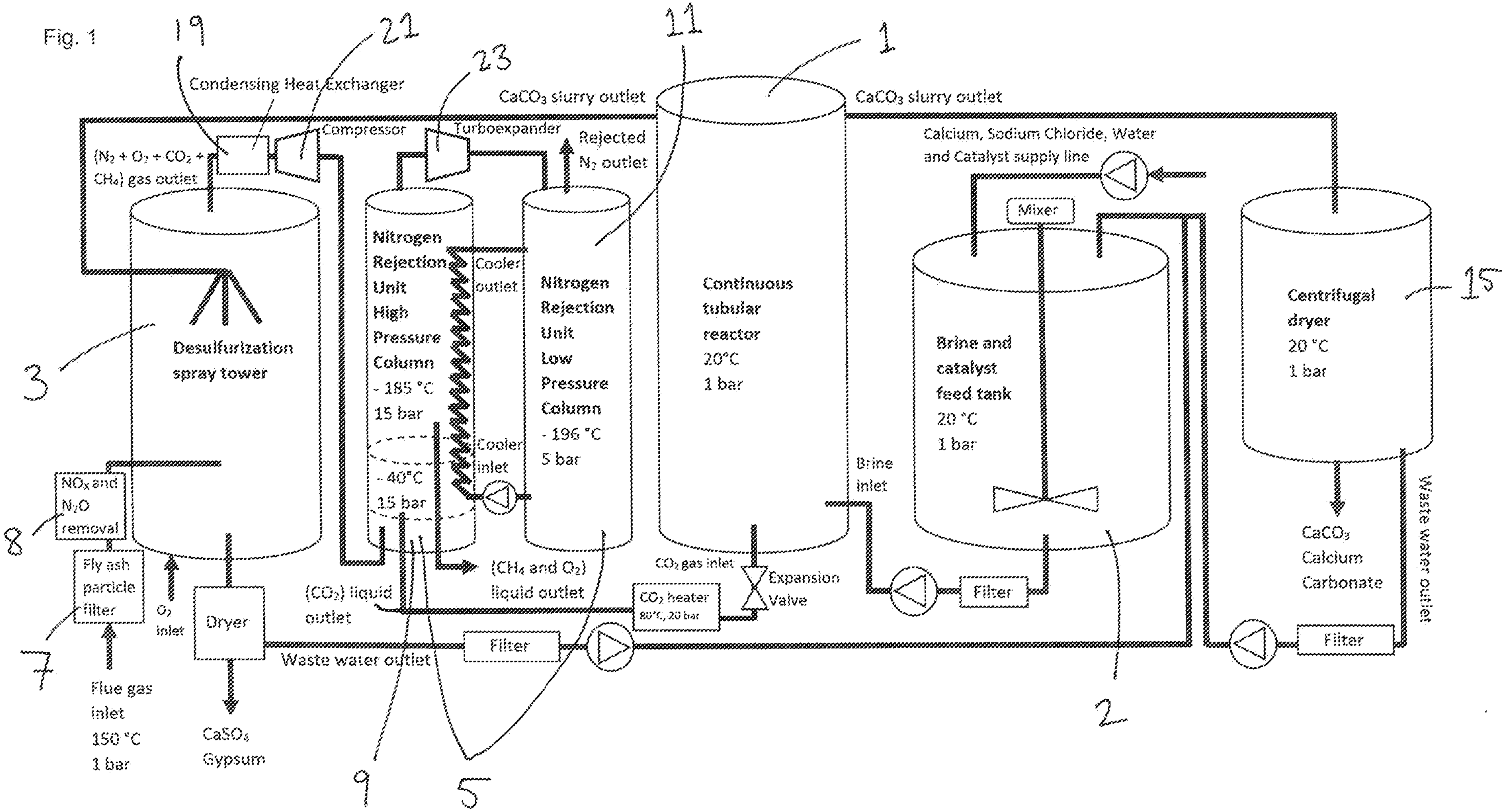

19
21
23
11
1
Condensing Heat Exchanger
Compressor
Turboexpander
CaCO₃ slurry outlet
CaCO₃ slurry outlet
Rejected N₂ outlet
(N₂ + O₂ + CO₂ + CH₄) gas outlet
Calcium, Sodium Chloride, Water and Catalyst supply line
Mixer
Nitrogen Rejection Unit High Pressure Column - 185 °C 15 bar
- 40°C 15 bar
Cooler outlet
Cooler inlet
Nitrogen Rejection Unit Low Pressure Column - 196 °C 5 bar
Continuous tubular reactor 20°C 1 bar
Brine and catalyst feed tank 20 °C 1 bar
Centrifugal dryer 20 °C 1 bar
15
3
Desulfurization spray tower
NOx and N₂O removal
8
Fly ash particle filter
7
O₂ inlet
Dryer
Flue gas inlet 150 °C 1 bar
CaSO₄ Gypsum
(CO₂) liquid outlet
(CH₄ and O₂) liquid outlet
CO₂ gas inlet
CO₂ heater 80°C, 20 bar
Expansion Valve
Brine inlet
Filter
Filter
Filter
Filter
Waste water outlet
Waste water outlet
CaCO₃ Calcium Carbonate
2
9
5

Fig. 2

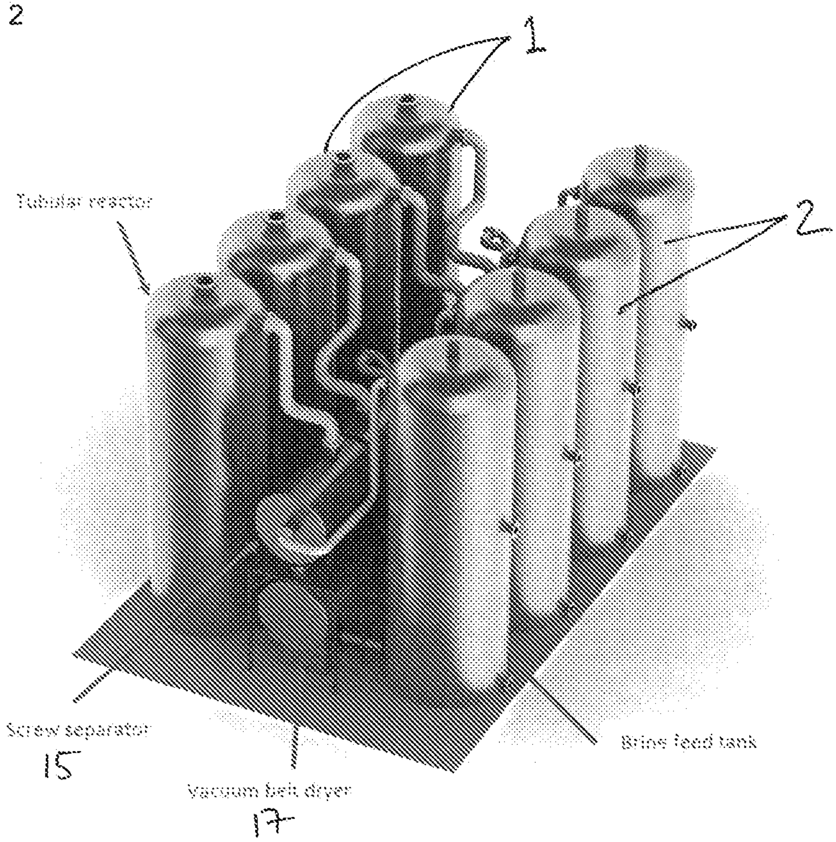

1
Tubular reactor
2
Screw separator
15
Vacuum belt dryer
17
Brine feed tank

Fig. 3

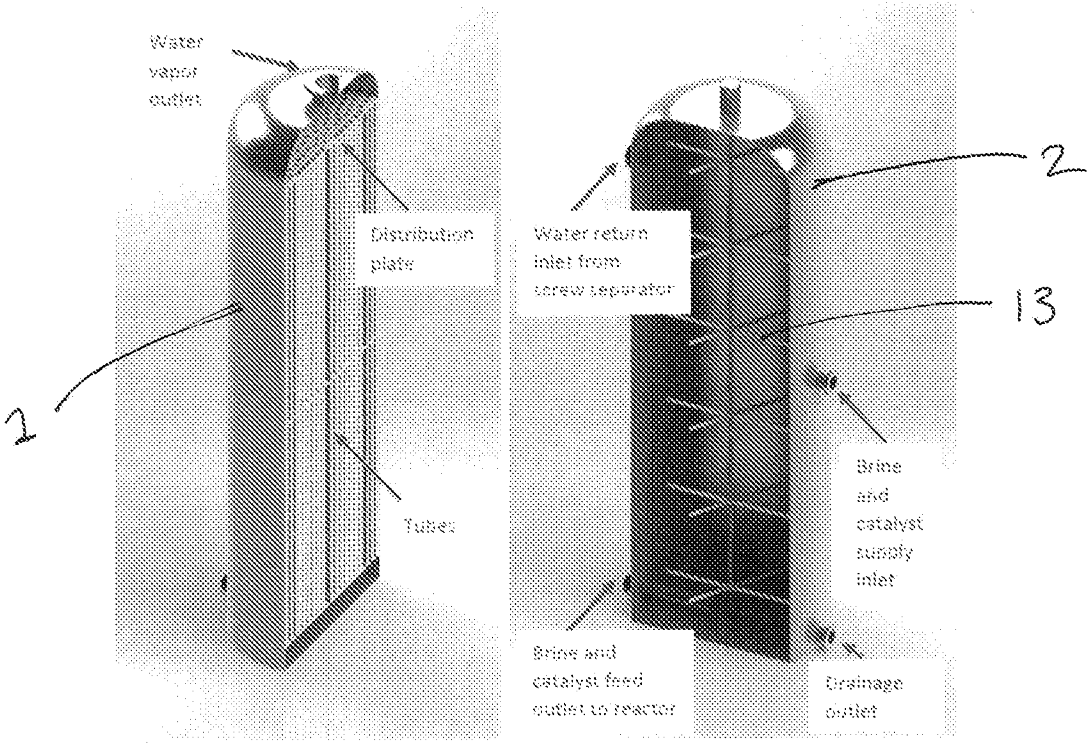

Water vapor outlet
Distribution plate
1
Tubes
2
Water return inlet from screw separator
13
Brine and catalyst supply inlet
Brine and catalyst feed outlet to reactor
Drainage outlet

Fig. 4

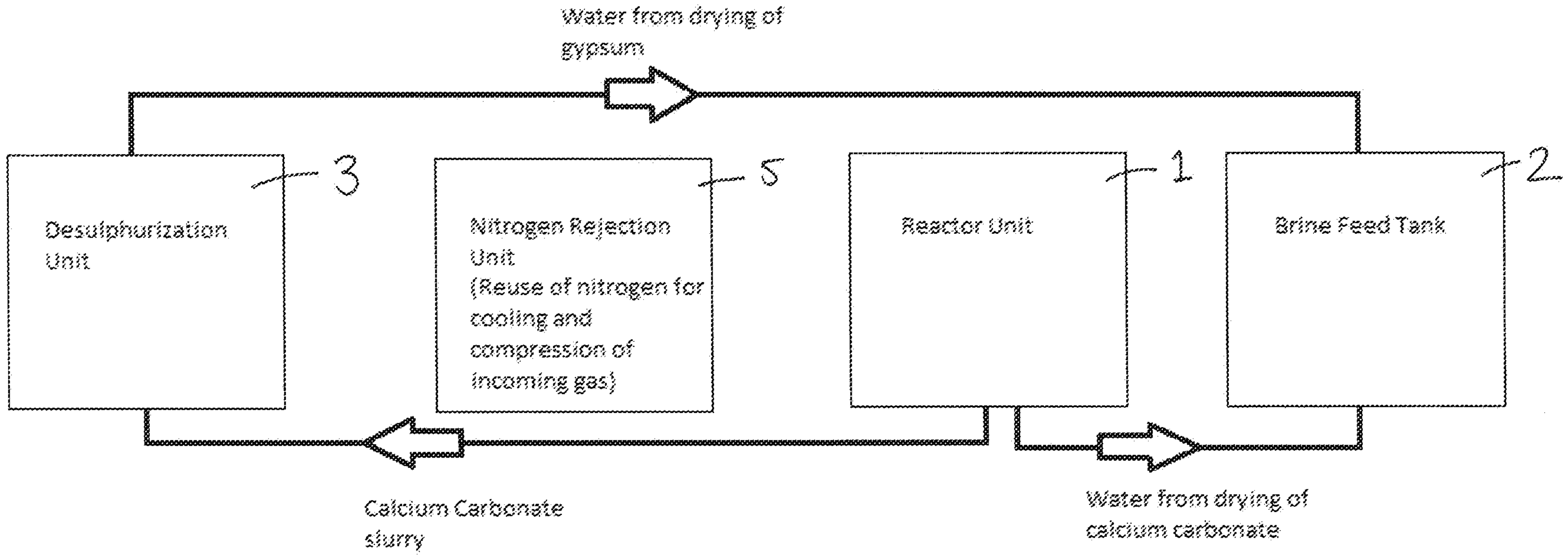

Water from drying of gypsum
Desulphurization Unit
3
Nitrogen Rejection Unit (Reuse of nitrogen for cooling and compression of incoming gas)
5
Reactor Unit
1
Brine Feed Tank
2
Calcium Carbonate slurry
Water from drying of calcium carbonate

Fig. 5

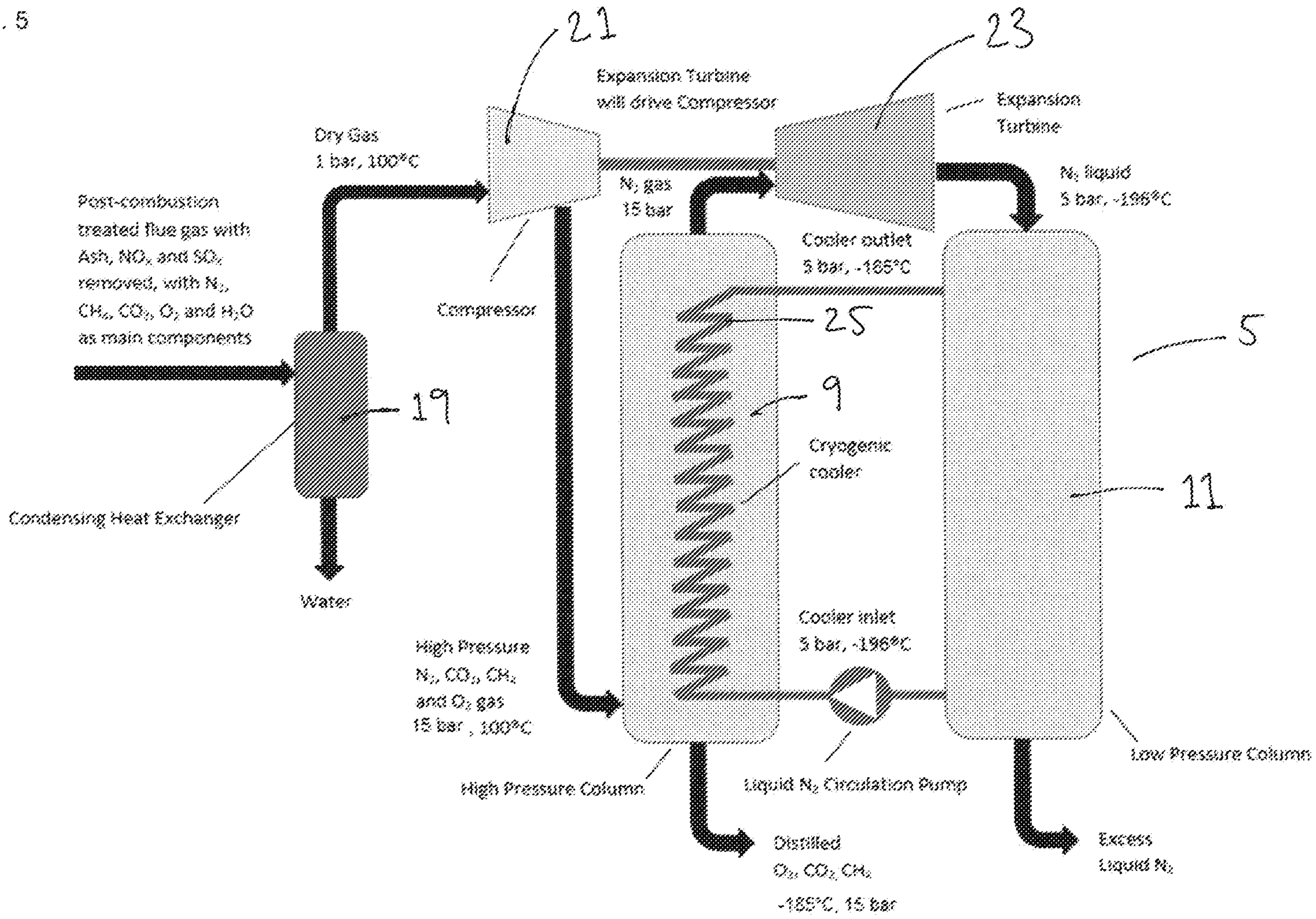

21
23
Expansion Turbine
will drive Compressor
Expansion
Turbine
Dry Gas
1 bar, 100°C
Post-combustion
treated flue gas with
Ash, NO_x and SO_x
removed, with N_2,
CH_4, CO_2, O_2 and H_2O
as main components
N_2 gas
15 bar
N_2 liquid
5 bar, -196°C
Compressor
Cooler outlet
5 bar, -185°C
25
5
19
9
Cryogenic
cooler
11
Condensing Heat Exchanger
Water
Cooler inlet
5 bar, -196°C
High Pressure
N_2, CO_2, CH_4
and O_2 gas
15 bar , 100°C
High Pressure Column
Liquid N_2 Circulation Pump
Low Pressure Column
Distilled
O_2, CO_2, CH_4
-185°C, 15 bar
Excess
Liquid N_2

Fig. 6

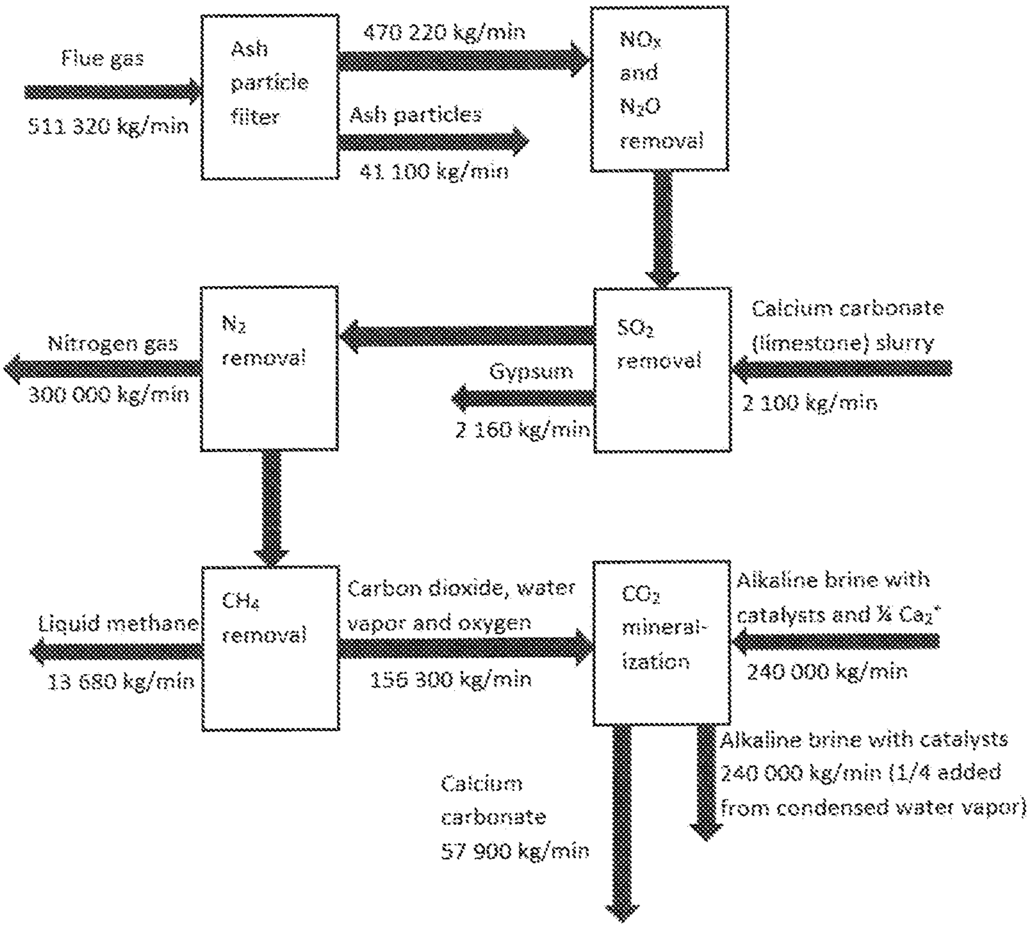
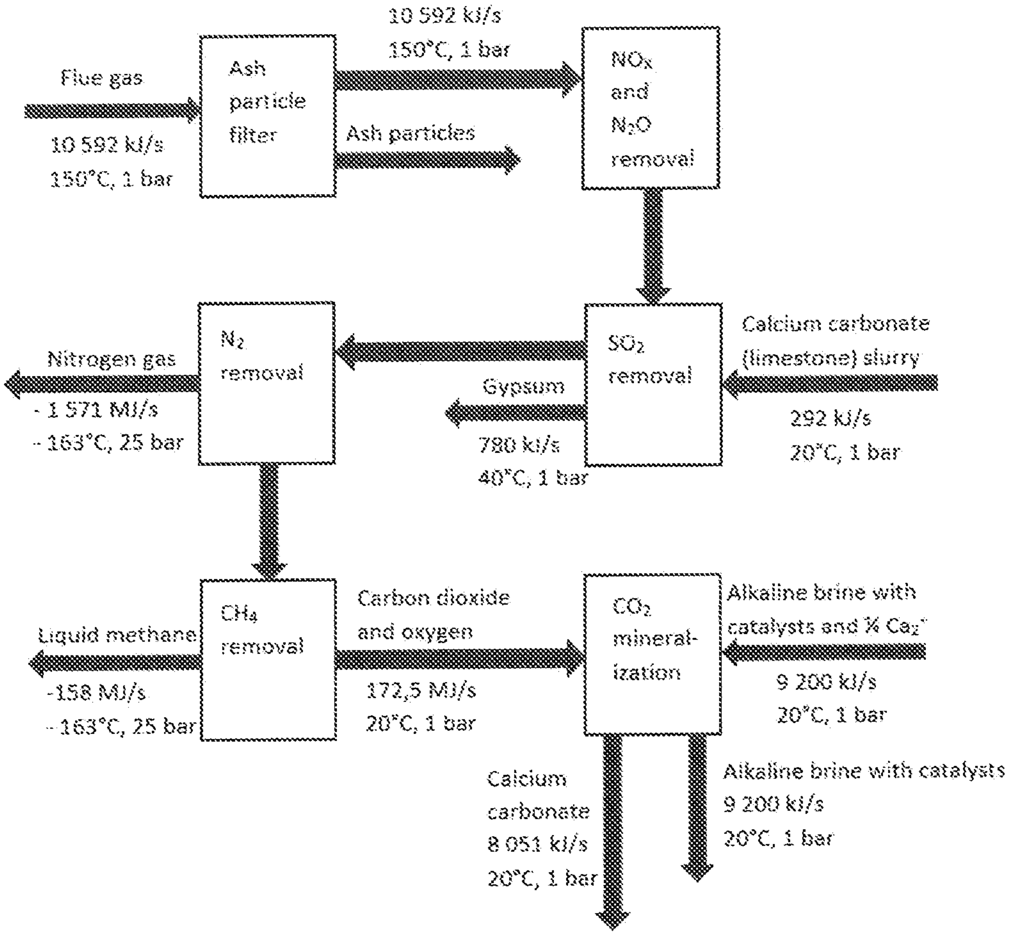

Flue gas
511 320 kg/min
Ash particle filter
470 220 kg/min
Ash particles
41 100 kg/min
NO_x and N_2O removal
SO_2 removal
Calcium carbonate (limestone) slurry
2 100 kg/min
Gypsum
2 160 kg/min
N_2 removal
Nitrogen gas
300 000 kg/min
CH_4 removal
Liquid methane
13 680 kg/min
Carbon dioxide, water vapor and oxygen
156 300 kg/min
CO_2 mineral-ization
Alkaline brine with catalysts and ¼ Ca_2^+
240 000 kg/min
Alkaline brine with catalysts 240 000 kg/min (1/4 added from condensed water vapor)
Calcium carbonate
57 900 kg/min

Fig. 7


Flue gas
10 592 kJ/s
150°C, 1 bar
Ash particle filter
10 592 kJ/s
150°C, 1 bar
Ash particles
NO_x and N_2O removal
SO_2 removal
Calcium carbonate (limestone) slurry
292 kJ/s
20°C, 1 bar
Gypsum
780 kJ/s
40°C, 1 bar
N_2 removal
Nitrogen gas
- 1 571 MJ/s
- 163°C, 25 bar
CH_4 removal
Liquid methane
-158 MJ/s
- 163°C, 25 bar
Carbon dioxide and oxygen
172,5 MJ/s
20°C, 1 bar
CO_2 mineral-ization
Alkaline brine with catalysts and ¼ Ca_2^{+}
9 200 kJ/s
20°C, 1 bar
Calcium carbonate
8 051 kJ/s
20°C, 1 bar
Alkaline brine with catalysts
9 200 kJ/s
20°C, 1 bar